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Internal motion of two-top molecules: propane and dimethylamine

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Two molecules with two internal rotors each (CH_3 group) were investigated by spontaneous Raman scattering. The torsional (overtone-) spectra yielded the relevant potential parameters for the internal motions. The potentials show characteristic differences due to the C_{2v} symmetry of propane and C_s symmetry of dimethylamine.

1. Introduction

At first glance, the two molecules in the title appear to be similar. They possess two methyl groups which can perform torsional motions around their symmetry axes. However, the symmetry of the molecules and the potential describing the internal motions are very different. Dimethylamine (DMA) can be thought of as an ammonia molecule with two hydrogen atoms replaced by CH_3 groups. The molecular symmetry group of DMA is G_{18} . The C–N–C plane does not contain the amino-hydrogen H_a [1]; this H_a can tunnel between two equivalent positions (an effect not considered in the present work). Propane (PRO) is much more symmetric (molecular symmetry group G_{36}); the two hydrogen atoms of the CH_2 group are placed symmetrically with respect to the C–C–C plane; consequently, fewer potential terms are needed to describe the motion of the two internal rotors [2].

It is customary (though not always sufficient, for certain degenerate irreducible representations of the appropriate molecular symmetry group) to distinguish between two twisting motions of the two CH_3

groups: the libration where both rotate to and fro in the same sense, ℓ_1 , the gearing motion; and their libration in the opposite sense, ℓ_2 , the anti-gearing motion. For PRO, only overtone excitation of these twisting modes is Raman-active, whereas for DMA, the ℓ_1 libration is also Raman-active for an excitation by a single torsional quantum.

The experimental apparatus consists of a very sensitive Raman spectrometer, an intracavity set-up with a signal gain of more than a factor 80 with respect to conventional extracavity measurements [2]. The achieved optimum resolution is 0.7 cm^{-1} fwhm for strong Raman transitions.

There exists much information on torsional spectra for molecules with two internal rotors. Especially Durig and co-workers have pioneered the field, also employing a Raman spectrometer [3]. The progress reported here comes mainly from the significantly improved sensitivity which allows the observation of transitions between levels where the upper one is near to the barrier hindering free rotation of the internal top. In this way, correlation effects between various potential parameters can be suppressed and the mutual interaction of the two tops can be discussed.

Table 1

Observed and calculated frequencies and intensities of torsional Raman overtone transitions of propane (cm^{-1})

Observed Raman shift	Observed relative intensity ^{a)}	Assignment $N''_{K''} \rightarrow N'_{K'}$	Calculated Raman shift	Observed Raman shift	Observed relative intensity ^{a)}	Assignment $N''_{K''} \rightarrow N'_{K'}$	Calculated Raman shift
369.6(1)	—	ν_9 , CCC-bend	—	693.7(3)	—	—	—
383.5(3)	sh	$1_2 \rightarrow 3_2$	383.23	702.8(3)	vw	$2_1 \rightarrow 6_1(\text{E}_3)$	703.32
393.4(2)	s	$2_1 \rightarrow 4_1$	393.58			$2_1 \rightarrow 6_2(\text{G})$	
412.5(1)	s	$1_1 \rightarrow 3_1$	412.39	708.5(3)	vw	$1_2 \rightarrow 5_2(\text{E}_1, \text{E}_4)$	708.21
423.0(1)	m	$0_1 \rightarrow 2_1$	423.05			$2_1 \rightarrow 6_2(\text{E}_2)$	
467.2(2)	s	$2_2 \rightarrow 4_4$	468.61	718.8(3)	vw	$3_2 \rightarrow 7_4(\text{A}_2)$	716.56
		$3_4 \rightarrow 5_6$				$3_2 \rightarrow 7_3(\text{G})$	
486.8(2)	vs	$1_1 \rightarrow 3_3$	487.56			$2_3 \rightarrow 7_1(\text{E}_3)$ ^{b)}	
		$2_3 \rightarrow 4_5$		728.4(3)	w	$1_2 \rightarrow 5_2(\text{A}_2, \text{G})$	728.82
506.2(1)	vs	$1_2 \rightarrow 3_4$	505.62	736.0(5)	—	—	—
521.2(1)	s	$0_1 \rightarrow 2_3$	521.61	748.6(3)	—	—	—
				758.6(3)	vw	$1_1 \rightarrow 5_1(\text{E}_2, \text{E}_3, \text{G})$	758.92
686.9(3)	w	$2_3 \rightarrow 6_3(\text{E}_1, \text{E}_3, \text{G})$	688.19				
		$3_1 \rightarrow 7_1(\text{A}_3)$					
		$3_1 \rightarrow 7_2(\text{G})$					

^{a)} vs=very strong, s=strong, m=medium, w=weak, vw=very weak, sh=shoulder.^{b)} The label 7_1 indicates a strongly mixed polyad level, with a strong admixture of the $N'=6$ polyad.

Table 2

Observed and calculated frequencies and intensities of torsional Raman transitions of dimethylamine (cm^{-1})

Observed Raman shift	Observed relative intensity ^{a)}	Assignment $N''_{K''} \rightarrow N'_{K'}$	Calculated Raman shift
176.6(7)	vvw	$1_2 \rightarrow 2_1$	176.93
235.2(4)	vw		
239.7(4)	vw		
243.2(7)	vw	$1_1 \rightarrow 2_2$	243.60
250.2(4)	w	$1_2 \rightarrow 2_3$	251.90
256.3(4)	w	$0_1 \rightarrow 1_2$	255.66
311.7(4)	w		
384.4(1)		ν_{12} , CNC-bend	
385.5(5)	sh		
390.7(4)	m	$3_1 \rightarrow 5_2(\text{E}_1, \text{E}_2)$	390.73
397.7(2)	m	$2_1 \rightarrow 4_1$	397.95
406.4(2)	s	$1_2 \rightarrow 3_2$	406.11
419.1(2)	s	$1_1 \rightarrow 3_1$	418.92
432.4(2)	s	$0_1 \rightarrow 2_1$	432.59
463.2(3)	m	$2_1 \rightarrow 4_3$	463.52
475.8(3)	m	$2_2 \rightarrow 4_4$	474.61
486.3(2)	s	$1_1 \rightarrow 3_3$	486.62
496.8(2)	s	$1_2 \rightarrow 3_4$	497.04
507.8(2)	s	$0_1 \rightarrow 2_3$	507.56

^{a)} s=strong, m=medium, w=weak, vw=very weak, vvw=very very weak, sh=shoulder.

Correlation between potential parameters occur when the experimental data are fitted, for low excitation energies, to the model Hamiltonian [4].

2. Theoretical aspects

The Hamiltonian is discussed for a non-rotating molecular frame, neglecting the tunnelling (inversion) motion of the H_a of DMA. The kinetic energy

Table 3

Torsional potential constants and kinetic coefficients (cm^{-1}). For DMA the errors are estimated; V'_3 is put equal to zero (see text)

	PRO		DMA	
	value	error	value	error
V_3	1353	2	1350	4
V_6	18.9	0.5	-7.3	0.5
V_+	-143	2	-123	4
V_-	-40.4	0.8	-131	2
V'_3	—	—	0	—
V'_6	—	—	104	1
V'_-	—	—	-365	3
F	5.72	0.01	6.69	0.04
F'	-1.58	0.02	-0.78	0.02

terms are given in ref. [2]; the potential energy contribution is

$$\begin{aligned}
 V(\alpha_1, \alpha_2) = & \sum_{k=1,2} \left[\frac{1}{2} V_3 (1 - \cos 3\alpha_k) \right. \\
 & + \frac{1}{2} (-1)^{k-1} V'_3 \sin 3\alpha_k + \frac{1}{2} V_6 (1 - \cos 6\alpha_k) \\
 & + \frac{1}{2} (-1)^{k-1} V'_6 \sin 6\alpha_k \left. \right] \\
 & + \frac{1}{2} V_+ [1 - \cos(3\alpha_1 + 3\alpha_2)] \\
 & + \frac{1}{2} V_- [1 - \cos(3\alpha_1 - 3\alpha_2)] \\
 & + \frac{1}{2} V'_- \sin(3\alpha_1 - 3\alpha_2) .
 \end{aligned} \quad (1)$$

Here α_k stands for the twisting angle of the k th rotor, $k=1, 2$. V_3 is the parameter that mainly determines the barrier of a single top. V_6 influences the width of the barrier. V_+ and V_- suffice to describe the rotor-rotor interaction in case of PRO. V_- (V_+) occurs as a factor of a cosine term which stays constant for the libration ℓ_2 (ℓ_1). (Note that these correspondences are due to the convention of sense of rotation, for the twisting angles α_k .)

In eq. (1), the terms with V'_- and V'_6 vanish for PRO; in case of DMA, however, they are of consid-

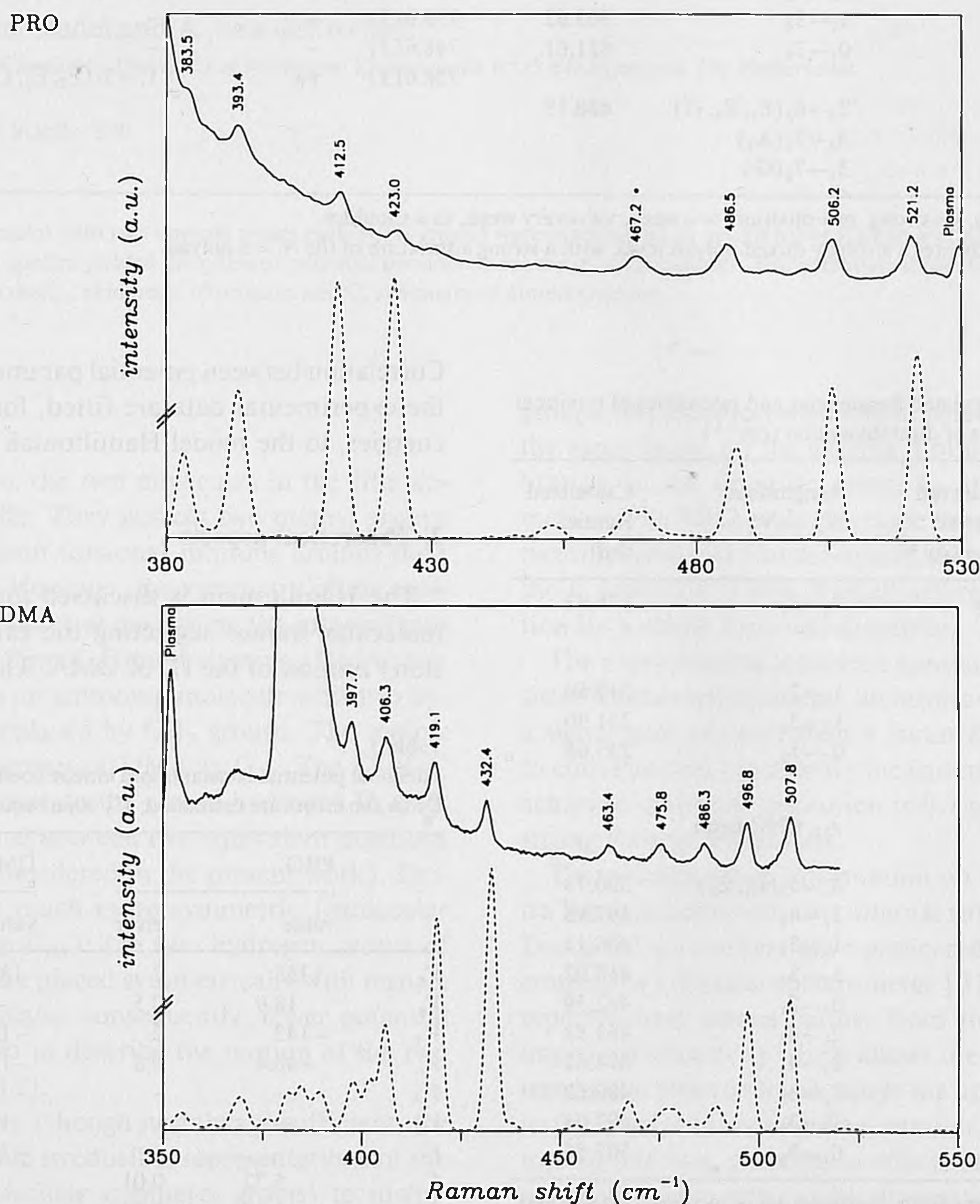


Fig. 1. $\Delta N=2$ torsional spectra for PRO and DMA. The calculated spectra are shown by dashed lines. In the DMA spectrum the strong peak at 384.4 cm^{-1} corresponds to the C-N-C bending mode (ν_{12}).

erable influence. As discussed in the introduction, their origin lies in the fact that the amino hydrogen is positioned out of the C-N-C plane. The parameter V'_3 has been put equal to zero, by an appropriate choice of the configuration at which $\alpha_1 = \alpha_2 = 0$ [4].

3. Results and discussion

The measured lines we found for PRO and DMA, together with an indication of their experimental strength and their assignment are shown in tables 1 and 2, respectively. N' (N'') stands for the number of torsional (librational) quanta present in the final (initial) state. $\Delta N = 1, 2$ or 4 denotes the number of quanta absorbed in the Raman transition. For PRO only overtones can be observed, $\Delta N = 2$ and 4. Those $N+1$ levels belonging to a fixed number N are said to belong to the same polyad; they are split by the interaction between the two tops. The subscript K (N'_K, N''_K) labels the different levels of each polyad. If the symmetry species is shown, (e.g. $N'(G)$) the transitions are resolved, for a defined symmetry type.

In general, the mutual top interaction mixes the states within a polyad, for instance three quanta in one rotor, zero in the other one, (3,0), and (2,1), (1,2) and (0,3). Where the mixing is minimal, the

transitions are stronger, since then the overlap between initial and final wavefunction is maximal.

For PRO this maximum overlap occurs for "vertical" transitions between levels of polyads either with the lowest-possible values of the K subscript or with the highest ones. Consequently, two series of strong $\Delta N = 2$ overtones (see fig. 1) are observed. For DMA there are more interaction terms in the potential leading to a more mixed situation [4]. The Raman intensity is spread out over more and weaker transitions and therefore the $\Delta N = 4$ ones become unobservable.

However, as discussed in the introduction, $\Delta N = 1$ transitions become Raman allowed so that a sufficient number of lines could be measured to achieve a satisfactory determination of the potential parameters in eq. (1) [5].

In table 3 these potential parameters are listed both for PRO and DMA. The potential barrier is comparable for both molecules. For DMA the mutual two-top potential (characterized by the parameters V_+ , V_- and V'_-) produces significant changes, especially through the term with V'_- , which is absent in case of propane. Remember, that from our measurements we cannot deduce how the one-top-minimum geometry $\alpha_1 = \alpha_2 = 0$ actually looks. The V_+ and V_- and V'_- terms drive the real minimum towards $\alpha_1 = -\alpha_2 = 2.8^\circ$. In addition, for the reflec-

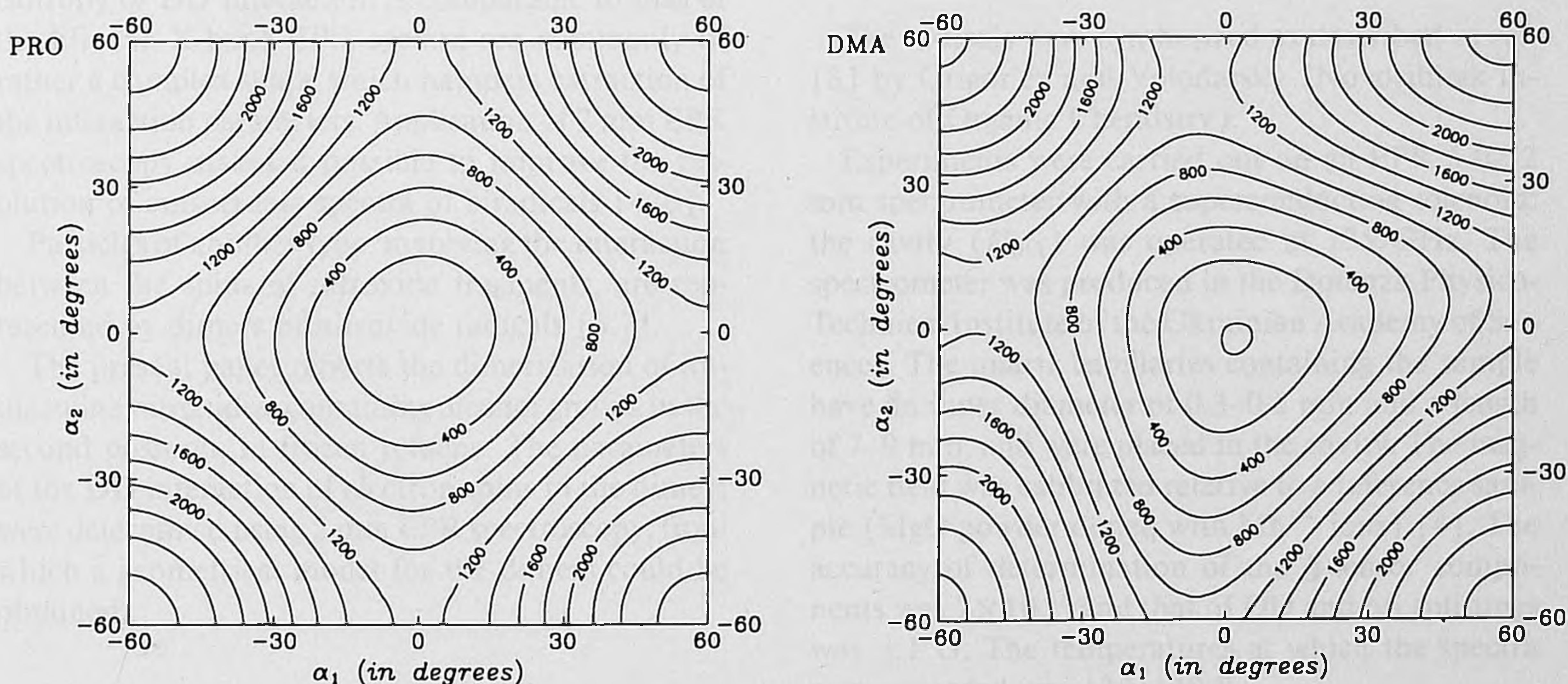


Fig. 2. Torsional potential for PRO and DMA. The numbers indicating the contour lines are energy values in wavenumbers.

tion $\alpha_1 \rightleftharpoons \alpha_2$ the potential becomes very asymmetric, see fig. 2.

In the case of DMA, the relatively large value of F is a consequence of kinetic correction [6]. These corrections add to the value of the rotational constant of a methyl group, rotating around its symmetry axis. Without kinetic corrections, for a rigid CH_3 -rotor the values 5.3 and 5.2 cm^{-1} are calculated for these rotational constants of DMA and PRO, respectively. The values F and F' (table 3) are obtained through a fit of the Hamiltonian to our experimental results.

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